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AD-A198 798

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER ARO 21783.11-CH	2. GOVT ACCESSION NO. N/A	3. RECIPIENT'S CATALOG NUMBER N/A
4. TITLE (and Subtitle) Reactions of Transition Metal Clusters with Simple Hydrocarbons		5. TYPE OF REPORT & PERIOD COVERED Final Report March 1, 1985 - May 31, 1988
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Michael A. Duncan		8. CONTRACT OR GRANT NUMBER(s) DAAG29-85-K-0040
9. PERFORMING ORGANIZATION NAME AND ADDRESS U of Georgia Athens, GA 30601		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS N/A
11. CONTROLLING OFFICE NAME AND ADDRESS U. S. Army Research Office Post Office Box 12211 Research Triangle Park, NC 27709		12. REPORT DATE 7/20/88
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

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17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

NA

18. SUPPLEMENTARY NOTES

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19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Metal clusters, photoionization, time-of-flight mass spectroscopy

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

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Reactions of Transition Metal Clusters with Simple Hydrocarbons

Final Report

July 20, 1988

U.S. Army Research Office
Contract No. DAAG29-85-K-0040

Michael A. Duncan

University of Georgia

Foreword

The enclosed final project report is for a contract funded from March 1, 1985 to May 31, 1988. Additional funding for this same research program was obtained through the DoD University Research Instrumentation Program (Grant No. DAAL03-87-G-0088).

A. Statement of the Problem Studied

Metal clusters are small aggregates of metal atoms which can be produced in molecular beam environments using laser vaporization pulsed nozzle techniques developed over the last several years. Such clusters are interesting because they provide model systems in which to study condensation phenomena, metal-metal bonding, metal-adsorbate bonding, and novel isomerism/rearrangement phenomena. Additionally, measurements of properties as a function of size probe the gradual trend from atomic and molecular behavior to bulk solid behavior. In the current project, various aspects of cluster electronic structure, metal bonding, and chemical reactivity have been considered. (mgm)

Clusters for all these experiments are produced in supersonic molecular beams by pulsed laser vaporization and are studied with various laser spectroscopy and mass spectroscopy methods. Condensation patterns are studied with laser photoionization of neutral clusters followed by time-of-flight mass spectroscopy mass analysis. Laser wavelength and power dependencies investigation photoionization dynamics. Corresponding positive and negative ion mass distributions are probed by pulsed time-of-flight sampling without photoionization. Cluster ion photodissociation energetics are studied in a reflectron type tandem time-of-flight spectrometer. Electronic spectroscopy and excited state dynamics are studied with resonant two-photon ionization spectroscopy. A flow reactor attached to the pulsed nozzle cluster source allows investigation of chemisorption reactions and their size dependence, with product analysis using mass spectroscopy. Overall, these are significant new experiments on metal systems with important implications for theoretical models of catalysis.

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B. Summary of Most Important Results

Our most significant results during the contract period have been in the general area of condensation phenomena and electronic structure of main group metal clusters. We have studied growth and photoionization dynamics in isovalent systems of group IV metals (tin, lead, germanium) and of pure group V semimetals (antimony and bismuth). Growth dynamics for antimony and bismuth have been studied as a function of charge. In all cases, isovalent cluster elements have very similar mass distributions. Other studies have investigated mixed clusters of the group IV-V metals (Sn/Bi, Pb/Sb, Sn/As) or of group III-V metals (In/Sb, In/Bi). In both systems mass spectra are characterized by highly non-statistical combinations of component elements with common patterns observed for all isovalent metal mixtures. Preferential stoichiometries in both alloy systems are predicted by a simple valence electron counting rule recognized in condensed phase inorganic chemistry. Taken together, these studies establish the first pattern in electronic structure for main group metal clusters in the gas phase.

Another ongoing area of research is the electronic structure of silver clusters. Using the new Nd:YAG laser system, photoionization has been studied for these clusters at a wide variety of ionization energies. Ionization potentials exhibit an even-odd alternation in the 5-6 eV energy range. No cluster smaller than 100 atoms has an IP less than 5.0 eV. Unusual resonances are observed for many different sized silver clusters in the 3-4 eV energy range. Mass spectral abundances exhibit marked deflections at 2, 8, and 20 valence-electron species. This same pattern has been observed for alkali metal clusters and is attributed to electronic shell closings in a spherical potential system.

A third project consists of high resolution UV spectroscopy on the silver trimer (Ag_3). Resonant two-photon photoionization has been used to obtain a UV excitation spectrum with sharp vibrational structure near 366 nm. Vibrational analysis establishes the structure of the system to be an equilateral triangle undergoing a dynamic Jahn-Teller interaction. Vibrational frequencies are 146 cm^{-1} for the symmetric stretch and 93 cm^{-1} for the bending mode, in good agreement with theory.

A final area of investigation has been tandem mass spectroscopy on metal clusters. In these experiments, one mass spectrometer mass selects a desired cluster species from the distribution produced initially. The tunable laser system is then used for energy adjusted photodissociation of the selected cluster. The second mass spectrometer analyzes the products of dissociation. These studies have examined the dynamics and energetics of dissociation for antimony and bismuth cluster cations and are currently being extended to bimetallic or mixed metal systems. In antimony and bismuth studies, preferential fragmentation products are the same molecules produced preferentially in cluster condensation. This observation again confirms the importance of the valence electron counting rule for predictions of cluster stability and electronic structure.

C. Publications Resulting from this Project

1. R. G. Wheeler and M. A. Duncan, "Neutral metal cluster formation and oxidation reactions in the photolysis of iron carbonyl van der Waals complexes," J. Phys. Chem. 90, 3876 (1986).

2. R. G. Wheeler, K. LaiHing, W. L. Wilson and M. A. Duncan, "Semi-metal clusters: Laser vaporization and photoionization of antimony and bismuth," Chem. Phys. Lett. 131, 8 (1986).

3. R. G. Wheeler, K. LaiHing, W. L. Wilson, J. D. Allen, R. B. King and M. A. Duncan, "Neutral gas phase analogs of condensed phase post-transition metal cluster ions: Laser vaporization and photoionization of Sn/Bi and Pb/Sb alloys," J. Am. Chem. Soc. 108, 8101 (1986).

4. K. LaiHing, R. G. Wheeler, W. L. Wilson and M. A. Duncan, "Photoionization dynamics and abundance patterns in laser vaporized tin and lead clusters," J. Chem. Phys. 87, 3401 (1987).

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6. R. G. Wheeler, K. LaiHing, W. L. Wilson and M. A. Duncan, "Laser vaporization and photoionization of group IV and V intermetallic clusters," in The Physics and Chemistry of Small Clusters, P. Jena ed., NATO ASI Series B, Plenum, New York, 1987.

7. K. LaiHing, P. Y. Cheng and M. A. Duncan, "UV photolysis in a laser vaporization cluster source: Synthesis of novel mixed-metal clusters," J. Phys. Chem. 91, 6521 (1987).

8. M. E. Geusic, R. R. Freeman and M. A. Duncan, "Photofragmentation of antimony and bismuth cations at 248 nm," J. Chem. Phys. 88, 163 (1988).

9. R. G. Wheeler, K. LaiHing, W. L. Wilson and M. A. Duncan, "Growth patterns in binary clusters of group IV and V metals," J. Chem. Phys. 88, 2831 (1988).

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11. M. A. Duncan and D. A. Rouvray, "Metal Clusters," Scientific American, in press.

12. M. B. Bishop, K. LaiHing, M. Peschke and M. A. Duncan, "Growth dynamics and photoionization processes in laser vaporized In/Sb and In/Bi intermetallic clusters," J. Phys. Chem., submitted.

13. K. LaiHing, P. Y. Cheng and M. A. Duncan, "Photoionization dynamics of silver clusters," in preparation.

14. P. Y. Cheng and M. A. Duncan, "Resonant two-photon ionization electronic spectroscopy of the silver trimer," in preparation.

15. K. LaiHing, P. Y. Cheng, N. Nevins, J. Plummer and M. A. Duncan, "Weakly bound complexes of metal atoms with rare gases and small molecules," in preparation.

D. Scientific Personnel Participating on this Project.

1. Professor Michael A. Duncan, Principle Investigator.

2. Professor Muriel B. Bishop, Visiting Faculty Associate (on sabbatical from Clemson University).

3. Kenneth LaiHing, graduate research assistant.

4. Robert G. Wheeler, graduate research assistant, awarded Ph.D. in Physical Chemistry, 8/87.

5. Po-Yuan Cheng, graduate research assistant.

6. Tracy G. Taylor, graduate research assistant.

7. Michael Peschke, graduate research assistant.

8. Kenneth Pearce, undergraduate research assistant.

9. James Plummer, undergraduate research assistant.

10. Neysa Nevins, graduate research assistant.

11. Jeff Allen, undergraduate research assistant.

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